Ph.D. Thesis

Ultrashort Pulsed Laser-Induced Chemistry: Methodology, Instrumentation, and Analysis

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Certificate of Original Authorship

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree. I also certify that the thesis has been written by me. Any and all help that I have received in my research work has been acknowledged. Finally, I certify that all information sources and literature used are indicated in the thesis.

Marcus Straw

Acknowledgements

The work presented in this dissertation was carried out under the supervision of Prof. Matthew Phillips, at the Microstructural Unit, Faculty of Science, University of Technology, Sydney, New South Wales, Australia. The work was performed within the Advanced Technology Group, Beam Technology R&D, FEI Company, Hillsboro, OR, U.S.A. I sincerely wish to thank Prof. Phillips for his guidance and support. I would also like to thank FEI Company for material support, Dr. Michael Lysaght for his support and flexibility, and Prof. Milos Toth for his review of my work and ongoing support throughout this process.

All work presented in the pages that follow was planned, coordinated, and managed exclusively by the author. As with any large project however, some degree of collaboration was required to achieve all that was achieved. I would like to take a moment here to explicitly acknowledge the work of those who contributed.

The instrumentation (see Figure 3.1) and experiments discussed in Chapter 3 were built and performed extensively by the author with the exception of the experiment using electron beam induced etching to illustrate the temperature dependence of surface adsorption (see Section 3.5.1). This experiment was suggested by Prof. Milos Toth and he did the EBIE work. The atomic force microscope line profiles shown in Figure 3.5 were collected by Dr. Steven Randolph.

The instrumentation (see Figure 4.1) and experiments detailed in Chapter 4 were likewise exclusively the work of the author with but two exceptions. First, the analysis of intensity data leading to the plot shown in Figure 4.5 was done by Dr. Jorge Filevich. Second, the author received a great deal of assistance from Dr. Steven Randolph setting up and learning to operate the quadrupole mass spectrometer portion of the instrumentation shown in Figure 4.10. Dr. Randolph was also instrumental in refining the subsequent experiments done to characterise the

by-products of the laser-induced plasma-mediated chemical reactions.

The development of the TripleBeam system has a long and storied history. It's hard to say definitively, but it is quite possible that the concept was first conceived by Dr. Mark Utlaut over a decade prior to the author's initial efforts. Dr. Utlaut was certainly the first to propose the idea within FEI Company and it is at FEI's world headquarters in Hillsboro, Oregon, USA that the earliest and the majority of the instrument's development has taken place. The first two prototypes of the tool were designed, built, and characterised almost exclusively by the author. The third and most current version has been a collaborative effort. The author's colleagues Mark Emerson, Dr. Steven Randolph, Dr. Jorge Filevich, and Dr. Aurélien Botman, as well as the author himself, all contributed variously to development of the LabView UI, alignment procedures, stage programming, beam stabilisation, contamination mitigation, optics, and beam delivery and control. In addition, elements of the most current design, particularly with regard to the laser injection port and the stage mount, were developed in collaboration with Dr. Tresa Pollock's group at the University of California, Santa Barbara in Santa Barbara, California, USA. This collaboration is discussed in more detail in Sections 5.6 and 5.7.

While the data collection and the segmentation work required to produce the three dimensional reconstruction of the geological sample presented in Section ref-sec:Gap was done solely by the author, the effort to quantify UPL-induced damage presented in the same section was a collaborative effort. Laser processing of tungsten carbide cobalt was done largely by Dr. Steven Randolph, while silicon processing was performed by the author. Transmission electron microscope and scanning transmission electron microscope analysis of these samples were performed by other FEI colleagues both in the U.S. and in Holland. Dr. Randolph also performed the electron backscatter diffraction analysis of UPL processed, single crystal copper discussed at the end of this section. Finally, the instrumentation, experiments, and analysis presented in Chapter 6 are the result of the collaborative efforts of the author and Dr. Randolph, and Dr. Randolph's contributions were considerable.

In addition to their critical technical support, I would like to offer special thanks to Dr. Steven Randolph, Dr. Mark Utlaut, Dr. Jorge Filevich, Dr. Milos Toth, and Dr. Aurélien Botman for the many, many useful discussions in which we engaged throughout this project's course.

Abstract

This dissertation explores the science and application of ultrashort pulsed lasers to locally induced chemical reactions having high spatial resolution. Chemical reactions driven in the gas phase by micro- to millimetre-scale plasmas formed when ultrashort pulsed laser ablation is performed in reactive gas atmospheres are studied via scanning electron microscopy, time-resolved optical emission spectroscopy, spatially resolved fast photography, plasma diagnostics, and mass spectrometry. Surface reactions resulting in metal deposition are explored via energy dispersive X-ray spectroscopy, electron backscatter diffraction, transmission electron microscopy, atomic force microscopy, and the use of a complex scientific instrument known as the TripleBeam designed and developed over the course of the project, and described in detail in this dissertation.

With wide scientific and industrial potential as both an experimental platform and a nanofabrication tool, the design and development of the TripleBeam instrument was initially motivated by the need to speed industrial processes currently employing focused ion beams. To that end, gas-phase ultrashort pulsed laser-induced chemistry was explored as a means of protecting sensitive components inside the instrument from material removed during in situ laser ablation. For this reason, reactions resulting in the transformation of solids to gas-phase compounds are targeted. However, a demonstration of the technique as a means for the fabrication of novel nanoparticles is also given.

Ultrashort pulsed laser-induced surface chemistries were explored with the hope of improving deposition rates and the purity of deposits made via electron and ion beam-induced processes. A previously unreported technique is presented in which electron-beam induced depositions provide templates for laser induced deposition, enabling both higher deposition rates and sub-diffraction limited pattern resolution.

With a rich potential application space driven by fundamental physics, ultrashort pulsed laser-induced chemistry can be seen as both an end in itself and as a means for exploring the complex interaction of light and matter. The work detailed in this dissertation produced methodologies, instrumentation, and analysis relevant to both the fundamental physics and the application of ultrashort pulsed-laser induced chemistry.

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List of Symbols and Abbreviations

α	optical absorption coefficient
$\Delta\tau$	ICCD gate delay
ν	photon frequency
ν_L	laser repetition rate
ϕ	laser fluence
ϕ_{th}	threshold laser fluence at which ablation occurs
τ_e	electron cooling time
τ_i	lattice heating time
τ_p	laser pulse duration
c	the speed of light
h	Planck's constant
k_B	Boltzmann constant
n_e	electron density
T_e	electron temperature
T_i	lattice temperature
v_g	group velocity
v_p	phase velocity

E_p laser pulse energy

a.u. arbitrary units

AFM atomic force microscope

APM additive pulse mode-lock

BSD backscattered electron detector

BSE backscattered electrons

BSS beam stabilisation system

CPA chirped pulse amplification

CW continuous wave

EBID electron beam-induced deposition

EBIE electron beam-induced etching

EBSD electron backscatter diffraction

EBSP electron backscatter pattern

EDS energy dispersive X-ray spectroscopy

ESEM environmental scanning electron microscope

ETD Everhart-Thornley secondary electron detector

FSM fast steering mirror

GIS gas injector system

GVD group velocity dispersion

HAZ heat affected zone

IBID ion beam-induced deposition

IBIE ion beam induced-etching

ICCD intensified charge coupled device

LCE laser chemical etch

LIBS laser-induced breakdown spectroscopy

LID laser-induced deposition

LIP laser injection port

LIPPS laser-induced periodic surface structures

LMIS liquid metal ion source

LTE local thermodynamic equilibrium

MCP microchannel plate

NA numerical aperture

ND neutral density

Nd:YAG neodymium-doped yttrium aluminium garnet laser gain medium

PE primary electrons

PLA pulsed laser ablation

RGA residual gas analyser

SE secondary electrons

SED secondary electron detector

SEM scanning electron microscope

SF_6 sulphur hexafluoride

SHG second harmonic generation

SiO_2 silicon dioxide

TE thermodynamic equilibrium

TEM transmission electron microscope

THG third harmonic generation

Ti:Sapphire titanium doped monocrystalline sapphire (Al_2O_3) laser gain medium

UI user interface

UPL ultrashort pulsed laser

UPLA ultrashort pulsed laser ablation

XeF_2 xenon difluoride